1554 *J. Chem. Eng. Data* **2004,** *49,* 1554−1559

Vapor−Liquid Equilibria of the Carbon Dioxide + Ethyl Propanoate and Carbon Dioxide + Ethyl Acetate Systems at Pressure from 2.96 MPa to 11.79 MPa and Temperature from 313 K to 393 K

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Vapor−liquid equilibrium data (p, T, x, ρ) for the carbon dioxide + ethyl propanoate (EP) and carbon dioxide + ethyl acetate (EA) systems were measured from 313 K to 393 K and in the pressure range from 2.96 MPa to 11.97 MPa. The measurements were carried out in a cylindrical autoclave with a moveable piston and an observation window. The results show that the solubilities of CO_2 in ethyl propanoate and ethyl acetate strongly increase with pressure, but the concentration of ethyl propanoate or ethyl acetate in the gas phase only slightly increases. The experimental data were correlated using the Peng−Robinson equation of state (EOS) with the two-parameter van der Waals mixing rule.

Introduction

Supercritical (SC) CO_2 is a nontoxic, nonflammable, and inexpensive solvent. In separation processes, it leaves no solvent residues in the products. The high diffusivity, low viscosity, and low surface tension of SC CO_2 speed up the mass transfer of the controlling chemical reactions. The solvent ability of SC CO_2 depends strongly on pressure and temperature. Thus, reaction mixtures or extracted materials can precipitate from the SC CO_2 only by pressure reduction. These separations then become gas−liquid or gas−solid separations, and large fractions of dilute liquid solvent in the downstream phase can be avoided. Products can be fractionated and purified directly from the mixtures without any solvent change. Because the heat of vaporization of CO_2 is only a small portion of the total energy needed to evaporate organic solvents or water, SC CO_2 extraction is energy efficient. From the mid-1980s, SC CO_2 + cosolvent (known as entrainer or modifier) systems have been of interest because they can increase the solubilities of biomaterials, medicines, and some components of Chinese herbal medicines[1−3] and natural flavors.

An accurate knowledge of phase behavior, especially vapor−liquid equilibria, is essential for the design, development, and operation of supercritical fluid separation processes. Vapor−liquid equilibrium data for several carbon dioxide + ester systems at high pressure have been previously reported.[4−6] The carbon dioxide + ethyl propanoate system has been measured only up to 323 K, and the carbon dioxide + ethyl acetate system has not been previously measured.

High-pressure vapor−liquid phase behavior for the carbon dioxide + ethyl propanoate and the carbon dioxide + ethyl acetate systems was investigated by using a cylindrical autoclave. Phase equilibrium data were measured from 313 K to 393 K and from 2.96 MPa to 11.97 MPa. The experimental data were fit with the Peng−Robinson equation of state using the two-parameter van der Waals mixing rule.

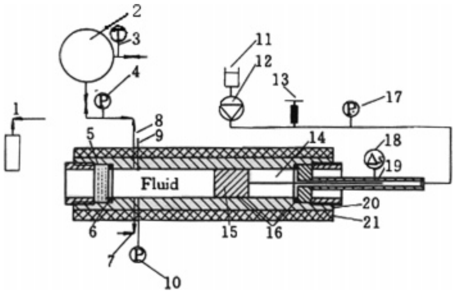

Figure 1. Schematic diagram of the high-pressure apparatus: 1, small steel vessel; 2, glass bulb; 3, thermometer; 4, pressure sensor; 5, window; 6, O-ring; 7, valve; 8, capillary; 9, thermocouple; 10, pressure sensor; 11, oil reservoir; 12, pump; 13, screw-driven pump; 14, oil; 15, piston; 16, O-ring; 17, pressure meter; 18, Hall probe; 19, magnet; 20, autoclave; 21, heat jacket.

Table 1. Pure-Component Parameters

compound	T_c/K	P_c/MPa	ω
ethyl propionate	546.05	3.32	0.391
ethyl acetate	523.55	3.78	0.362
carbon dioxide	304.2	7.38	0.225

Experimental Section

Materials. Instrumental-grade carbon dioxide with a purity of 99.99 mass % was obtained from the Jinjing Gas Company. Ethyl propanoate and ethyl acetate were obtained from Acrose Organics with a minimum purity of 99 mass %. The carbon dioxide was dried with P_2O_5 powder, and the esters were used without further purification; however, they were degassed for 2 h at low temperature (273 K).

Experimental Apparatus and Procedures. The type of experimental apparatus used for the vapor−liquid equilibrium measurements has been described by Lentz and Zeuner[7] and is shown in Figure 1. The key part of the apparatus is a cylindrical high-pressure autoclave (o.d. 78 mm, i.d. 22 mm, maximum internal volume 100 cm^3). It was built from a special alloy (1Cr18Ni9Ti). A piston separates the contents of the autoclave from a pressure medium that was used to move the piston to generate the pressure inside the autoclave. A quartz window allows the observation of the phase behavior of the contents. The window and the piston are each sealed with an O-ring

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10.1021/je034224j CCC: $27.50

Table 2. (a) Vapor−Liquid Phase Equilibrium Data of the SC CO_2(1) + EP(2) and SC CO_2(1) + EA(2) Systems at Various Temperatures and Pressures

SC CO_2(1) + EA(2)

p/MPa	x_{CO2}	ρ_l/g·cm^{-3}	y_{CO2}	ρ_g/g·cm^{-3}
$T = 313$ K				
2.96	0.5818	0.9710	0.9933	0.0660
3.96	0.6881	0.9736	0.9968	0.1018
4.46	0.7509	0.9659	0.9978	0.1106
4.96	0.7990	0.9609	0.9980	0.1368
5.46	0.8301	0.9509	0.9970	0.1887
5.97	0.8675	0.9233	0.9961	0.2484
6.27	0.8871	0.9024	0.9956	0.2799
$T = 333$ K				
2.96	0.4093	0.9002	0.9963	0.0524
3.46	0.4733	0.9053	0.9961	0.0629
4.46	0.5479	0.9029	0.9945	0.0940
5.46	0.6214	0.8955	0.9929	0.1235
5.96	0.6608	0.8866	0.9910	0.1461
6.66	0.7224	0.8687	0.9905	0.2018
7.26	0.7819	0.8422	0.9900	0.2616
$T = 353$ K				
2.96	0.3557	0.8644	0.9930	0.0484
3.86	0.4093	0.8649	0.9900	0.0679
4.96	0.4746	0.8691	0.9891	0.0923
5.96	0.5459	0.8551	0.9860	0.1162
6.96	0.6173	0.8540	0.9820	0.1485
7.97	0.6847	0.8505	0.9742	0.1954
8.87	0.7529	0.8243	0.9722	0.2698
$T = 373$ K				
2.96	0.3282	0.8170	0.9813	0.0444
4.46	0.3961	0.8124	0.9755	0.0686
5.96	0.4965	0.8021	0.9729	0.1045
7.47	0.5422	0.7882	0.9725	0.1340
8.97	0.6332	0.7667	0.9626	0.2177
10.57	0.7127	0.7357	0.9545	0.3590
10.97	0.7391	0.7209	0.9464	0.3922

SC CO_2(1) + EA(2)

p/MPa	x_{CO2}	ρ_l/g·cm^{-3}	y_{CO2}	ρ_g/g·cm^{-3}
$T = 333$ K				
5.36	0.5727	0.8657	0.9877	0.1231
5.96	0.6283	0.8363	0.9860	0.1544
6.47	0.6584	0.8148	0.9861	0.1698
7.57	0.7586	0.7853	0.9787	0.2068
8.46	0.8057	0.7467	0.9736	0.2731
8.97	0.8421	0.7204	0.9696	0.3708
$T = 353$ K				
3.96	0.5532	0.9232	0.9802	0.0666
5.06	0.5767	0.9209	0.9783	0.0935
6.27	0.6075	0.9196	0.9739	0.1270
7.47	0.6270	0.9017	0.9678	0.1822
8.47	0.6668	0.8540	0.9661	0.2200
9.47	0.7587	0.7465	0.9560	0.2634
$T = 373$ K				
5.69	0.4697	0.7588	0.9641	0.0819
6.46	0.5001	0.7843	0.9612	0.1202
7.96	0.5505	0.7905	0.9555	0.1682
9.47	0.6046	0.7817	0.9440	0.2401
10.57	0.6715	0.7884	0.9239	0.3520
11.37	0.7259	0.7803	0.9135	0.4692
$T = 393$ K				
5.06	0.4550	0.7137	0.9516	0.0550
5.46	0.4831	0.7448	0.9419	0.0849
6.97	0.5129	0.7711	0.9321	0.1218
8.48	0.5450	0.8043	0.9173	0.1766
9.97	0.5744	0.7918	0.8956	0.2550
11.47	0.6237	0.7558	0.8568	0.4000
11.97	0.6629	0.7197	0.8466	0.6025

(silicone rubber). For better mixing, the contents of the autoclave were magnetically stirred. The pressure was generated either mechanically by a pump or manually by a screw-driven pump. It was measured with a pressure sensor. The temperature of the autoclave was adjusted using a heating jacket and was measured by a calibrated chromel-to-alumel thermocouple inside the cell. The total uncertainty of the pressure was ±0.01 MPa, and the total uncertainty of the temperature was ±0.1 K.

After filling the cell with CO_2 and esters, we adjusted the temperature to the desired value and then adjusted the pressure. Phase equilibrium, indicated by reaching a constant p and the absence of the boiling of the condensing phase inside the cell, was typically reached 2 h after the termination of stirring. After adjusting the phase equilibrium to a given p and T, we removed samples of the liquid and gas phases using the upper and lower valves, respectively, and then placed into a previously evacuated and weighed small steel vessel through a needle valve. During this process, the pressure inside the autoclave was kept constant by pushing the piston toward the chamber with the screw-driven pump. The total mass of the samples was measured by using a balance with an accuracy of 0.0001 g. The volume of the sample taken was determined by measuring the distance between the positions of the piston before and after taking the sample, Δl, and the diameter of the autoclave. The positions of the piston were measured with the help of a Hall probe connected to the piston. The uncertainty of Δl was ±0.1 mm. The densities of the samples were determined using the ratio of the weights to the volume of the sample. The cooled vessel was connected to a previously evacuated glass bulb of known volume, and then the CO_2 in the sample was allowed to flow into the glass bulb. The bulb's temperature was at room temperature and was measured with a thermometer. The pressure of CO_2 inside the glass bulb was measured with an absolute-pressure sensor with an accuracy of 10 Pa. Because the pressure of the CO_2 inside the bulb is very low (typically 20 kPa), the number of moles of CO_2 was easily calculated using the ideal gas equation of state. The mass of CO_2 was also calculated using a weight difference method. The mass of the ester is the difference between the total mass of sample taken and the mass of the CO_2. Finally, the mole fraction of the two phases could be obtained for the given p and T. The temperature was measured with an accuracy of 0.1 K, and the accuracy in pressure varied between $0.001p$ and $0.004p$. The error in density, ρ, was ±0.0001 g·cm^{-3}. The molar fractions of the two systems were determined with an error of <0.001.

Correlations

The experimental data were correlated with the Peng−Robinson equation of state and the conventional mixing rules.

The Peng−Robinson equation of state has the following form:

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{1}$$

The variables p, T, and V_m represent the pressure, temperature, and molar volume, respectively.

For a pure fluid, constant b is given by

$$b = 0.077780\frac{RT_c}{p_c} \tag{2}$$

whereas $a(T)$, a function of temperature, is given by

$$a(T) = a(T_c)\ \alpha(T_r,\omega) \tag{3}$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{p_c} \tag{4}$$

$$\alpha(T_r, \omega) = [1 + k(1 - T_r^{0.5})]^2 \tag{5}$$

The variables T_c, T_r, and p_c represent the critical temperature, relative temperature, and critical pressure.

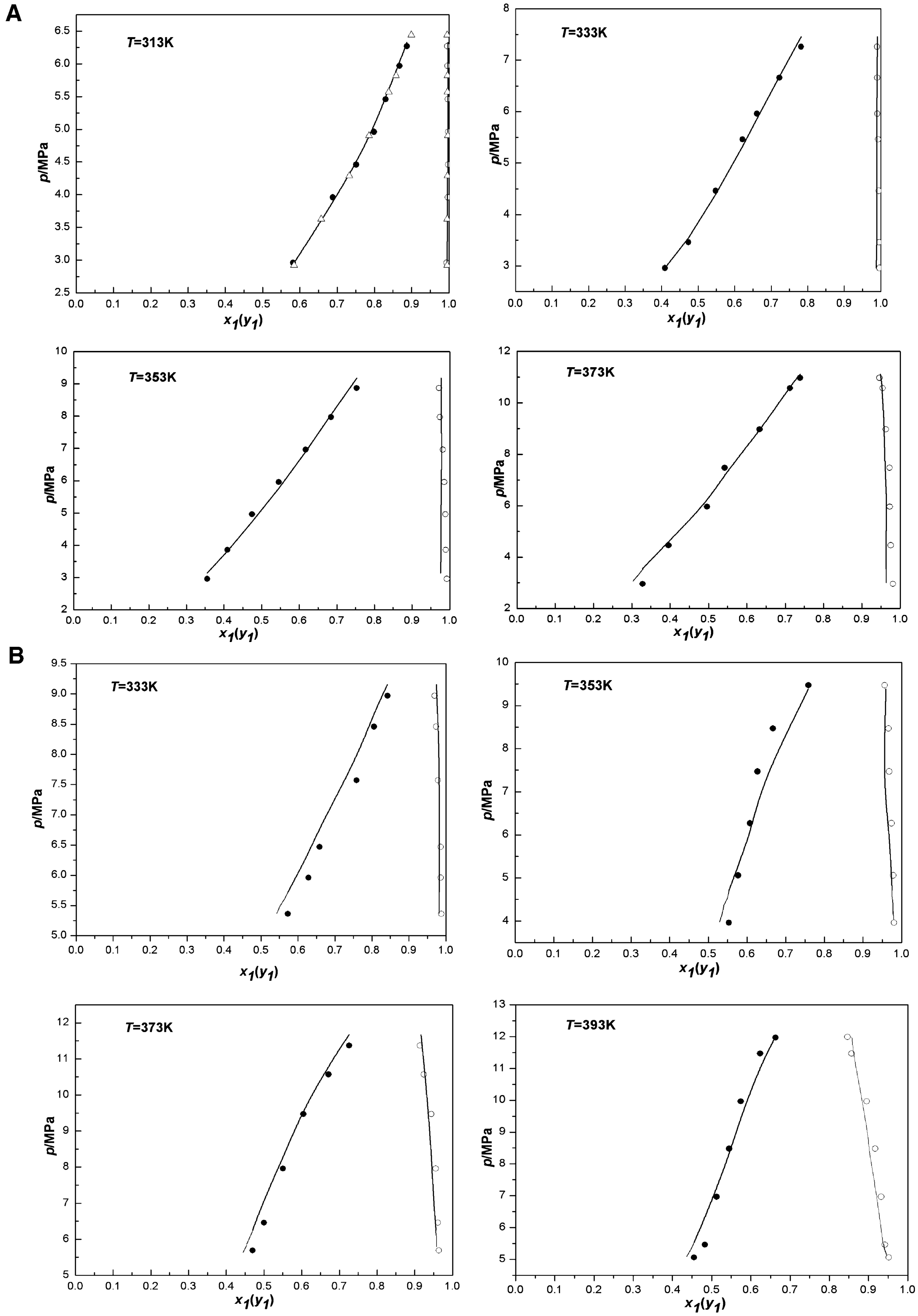

Figure 2. (a) $p-x_1(y_1)$ diagram of the carbon dioxide (1) + ethyl propanoate (2) system at four temperatures: ● ○, experiment; −, fitted; △, literature.[13] Solid points represent the liquid phase, and unfilled symbols represent the gas phase. (b) $p-x_1(y_1)$ diagram of the carbon dioxide (1) + ethyl acetate (2) system at four temperatures: ● ○, experiment; −, fitted. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

Here, $T_r = T/T_c$ and k depends on the acentric factor, ω, according to

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (6)$$

The critical data ($p_{c,i}$, $T_{c,i}$) were taken from the literature,[10] and the acentric factors (ω's) can be obtained by fitting the functions to vapor pressure data.[11] Table 1 summarizes these constants for the studied components.

For a binary mixture, the common procedure is to write mixing rules that are quadratic in mole fraction:

$$b_M = g_1^2 b_1 + g_2 b_2 + 2g_1 g_2 b_{12} \qquad (7)$$

$$a_M = g_1^2 a(T) + 2g_1 g_2 a_{12}(T) + g_2^2 a_2(T) \qquad (8)$$

where g is either x or y.

$a_1(T)$ (or $a_2(T)$) and b_1 (or b_2) refer to the pure-component values, and b_{12} and $a_{12}(T)$ are binary interaction parameters. It is convenient to express these in the form

$$b_{12} = \frac{1}{2}(b_1 + b_2)(1 - c_{12})$$

$$a_{12}(T) = [a_1(T)\, a_2(T)]^{0.5}(1 - k_{12})$$

where c_{12} and k_{12} are adjustable parameters and depend on temperature.

The fugacity coefficient ϕ_i for a component i in a mixture is given by

$$\ln \phi_i = \frac{b_i}{b_{\mathrm{M}}}\left(\frac{pV_{\mathrm{m}}}{RT} - 1\right) - \ln \frac{p(V_{\mathrm{m}} - b_{\mathrm{M}})}{RT} - \frac{a_{\mathrm{M}}}{2\sqrt{2}b_{\mathrm{M}}RT}\left[\frac{2\sum_i g_i a_{12}}{a_{\mathrm{M}}} - \frac{b_i}{b_{\mathrm{M}}}\right] \ln \frac{V_{\mathrm{m}} + (1 + \sqrt{2})b_{\mathrm{M}}}{V_{\mathrm{m}} + (1 - \sqrt{2})b_{\mathrm{M}}} \qquad (9)$$

For a binary liquid mixture at temperature T and pressure p with mole fractions x_1 and x_2 in equilibrium with its vapor with mole fractions y_1 and y_2, the equations of equilibrium are

$$f_1^{\mathrm{v}} = f_1^{\mathrm{l}} \text{ or } \phi_1^{\mathrm{v}} y_1 = \phi_1^{\mathrm{l}} x_1 \qquad (10)$$

and

$$f_2^{\mathrm{v}} = f_2^{\mathrm{l}} \text{ or } \phi_2^{\mathrm{v}} y_2 = \phi_2^{\mathrm{l}} x_2 \qquad (11)$$

Results and Discussion

Isothermal vapor−liquid equilibrium data were measured at 313 K, 333 K, 353 K, and 373 K over the pressure range from 2.96 MPa to 10.97 MPa for the CO_2 + ethyl propanoate system and at 333 K, 353 K, 373 K, and 393 K over the pressure range from 3.96 MPa to 11.97 MPa for the CO_2 + ethyl acetate system. These results are given in Table 2, where $x(CO_2)$ and $y(CO_2)$ are the mole fractions of CO_2 in the liquid phase and vapor phase, respectively. ρ(l) and ρ(g) are the densities of the two phases, respectively. The $p-x, y$ diagram is shown in Figure 2. The lines represent the isotherms fit with the Peng−Robinson equation using the van der Waals mixing rule. For the CO_2 + ethyl propanoate system, the experimental data obtained by Wagner[13] at 313 K are also shown. The agreement between this work and the literature values is quite satisfactory. Parts a and b of Figure 2 have been modified to include the data points from Wagner and the current work. The data were compared with the results of the correlation equation. The errors were all within the range of ±1.0%. It should be noted that Wagner used the Soave−Redlich−Kwong equation with satisfactory results at low temperature, but the results were not good at higher temperature. Therefore, we used the Peng−Robinson EOS, which gives good results at all of the studied temperatures. The measured results show that the solubility of CO_2 in ethyl propanoate and the concentration of ethyl propanoate in the gas phase both increase with elevated pressure.

Parts a and b Figure 3 give the isothermal $p-\rho$ curves. The density of the gas phase increases with elevated pressure, but the density of the liquid phase decreases with pressure. The mixture mole volumes of CO_2 in the gas and liquid phases at different T and p can be obtained from the densities and mole fractions. Those results are shown in Figure 4a and b. The thin lines connecting the conjugate points in the two phases are isobars.

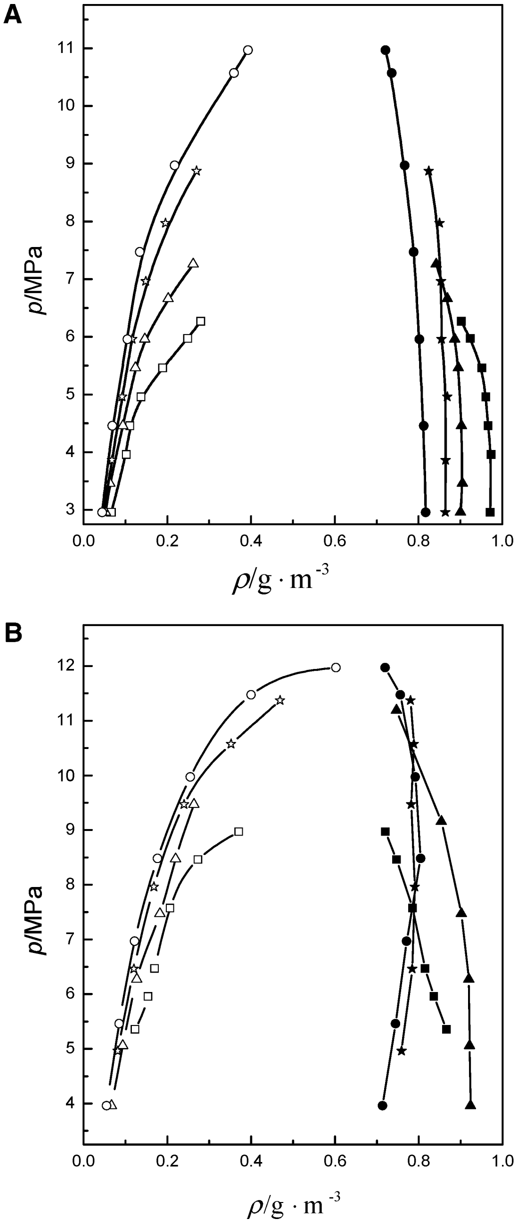

Figure 3. (a) $p-\rho$ diagram of the carbon dioxide + ethyl propanoate system at four temperatures: ■ □, 313 K; ▲ △, 333 K; ★ ☆, 353 K; ● ○, 373 K. Solid points represent the liquid phase, and unfilled symbols represent the gas phase. (b) $p-\rho$ diagram of the carbon dioxide + ethyl acetate system at four temperatures: ■, □ 333 K; ▲ △, 353 K; ★ ☆, 373K; ● ○, 393 K. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

The criterion for phase equilibrium requires that multiple phases at the same T and p must be in equilibrium and the fugacity of each component must be the same in all phases. The fitting was performed at each temperature by minimizing the following objective function

$$E = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{p_{\mathrm{exptl}} - p_{\mathrm{calcd}}}{p_{\mathrm{exptl}}}\right) + \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{y_{\mathrm{exptl}} - y_{\mathrm{calcd}}}{y_{\mathrm{exptl}}}\right)^2 \qquad (12)$$

where the subscripts exptl and calcd represent experimental and calculated values, respectively.

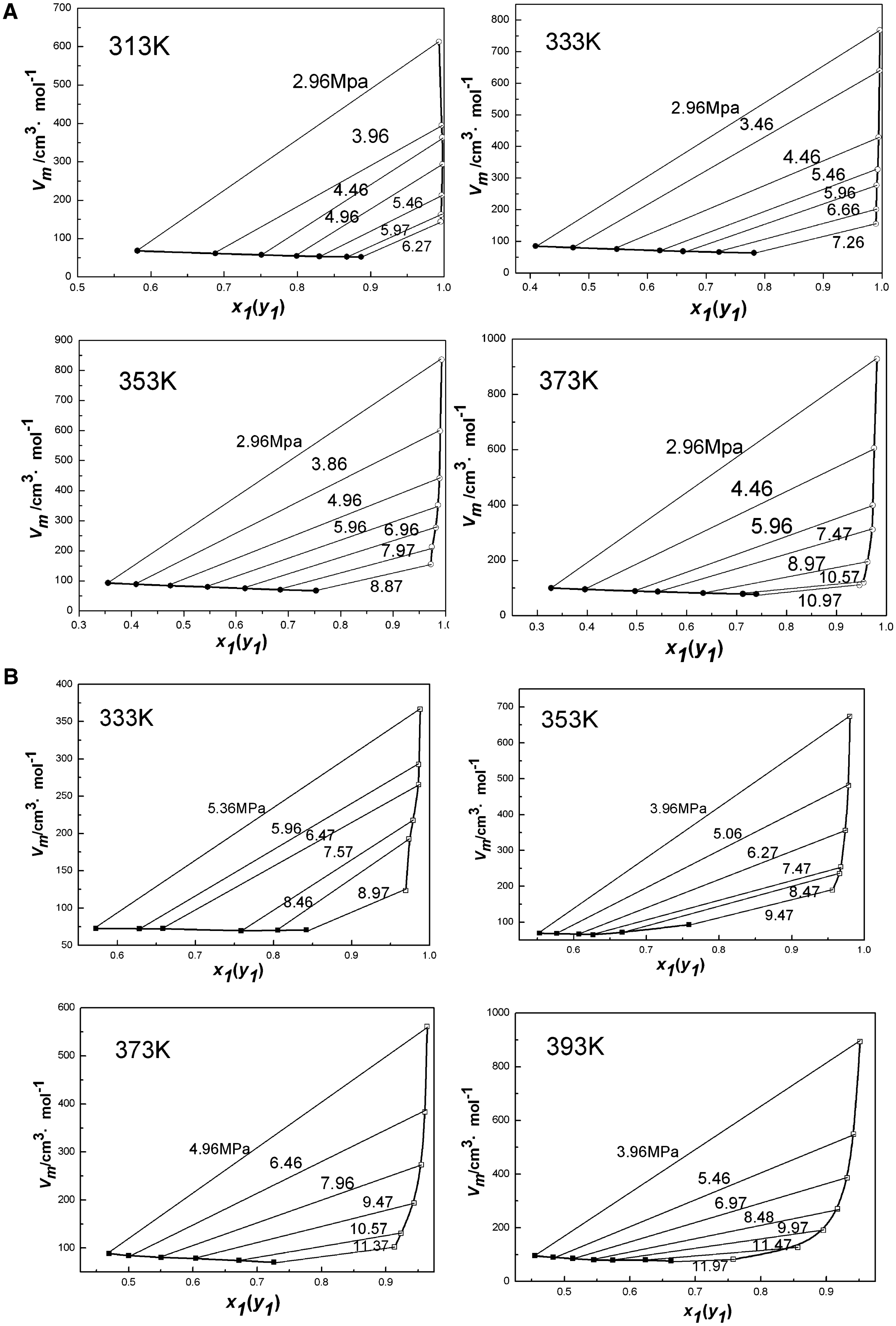

Figure 4. (a) V_m–$x(y)$ diagrams of the carbon dioxide + ethyl propanoate system at different temperatures. Solid points represent the liquid phase, and unfilled symbols represent the gas phase. (b) V_m–$x(y)$ diagrams of the carbon dioxide + ethyl acetate system at different temperatures. Solid points represent the liquid phase, and unfilled symbols represent the gas phase.

In this work, the experimental data were correlated using the Peng–Robinson EOS with different mixing rules. The results show that the Peng–Robinson EOS with the two-parameter van der Waals mixing rule correlates with the experimental data fairly well. The fitted c_{12} and k_{12} parameters for the two systems at different temperatures are summarized in Table 3, and the average relative errors (ARE) of $p(p_{\mathrm{exptl}} - p_{\mathrm{calcd}}/p_{\mathrm{exptl}})$ and $y(y_{\mathrm{exptl}} - y_{\mathrm{calcd}}/y_{\mathrm{exptl}})$ are also given. From Table 3, it can be seen that the values of k_{12} and c_{12} are all very small. The nonzero c_{12} value shows that the systems are asymmetric, and the small k_{12} value indicates that the interaction forces between the small

Table 3. Fitted Results for Two Systems SC CO_2(1) + EA(2) and SC CO_2(1) + EP(2)

SC CO_2(1) + EA(2) system					SC CO_2(1) + EP(2) system				
T/K	k_{12}	c_{12}	p_{ARE}%	y_{ARE}%	T/K	k_{12}	c_{12}	p_{ARE}%	y_{ARE}%
333	0.02	0.08	1.60	0.46	313	−0.09	−0.10	3.84	0.22
353	−0.14	0.11	7.73	0.77	333	−0.05	0.05	4.44	0.46
373	0.01	0.09	4.25	1.20	353	−0.06	0.09	11.06	0.93
393	−0.08	0.05	8.94	3.99	373	−0.05	0.07	9.46	0.84

esters and carbon dioxide are very weak. From Table 3, it can also be seen that parameters k_{12} and c_{12} do not have a definite trend with temperature.

Literature Cited

(1) Wong, J. M.; Johnston, K. P. Solubility of Biomolecules in Carbon Dioxide Based Supercritical Fluids. *Biotechnol. Prog.* **1986**, *2*, 29−32.

(2) Schaffer, S. T.; Zalkowl, H.; Teja, A. S. Solubility of Monocrotaline in Supercritical Carbon Dioxide and Carbon Dioxide+Ethanol Mixtures. *Fluid Phase Equlib.* **1988**, *43*, 45−48.

(3) Knez, Z.; Skerget, M. Phase equilibria of the vitamins D_2, D_3 and K_3 in binary systems with CO_2 and propane. *J. Supercrit. Fluids* **2001**, *20*, 131−144.

(4) Williams, L.; Eric, M.; Rubin, J. B. Vapor−Liquid Equilibrium in the Carbon Dioxide−Propylene Carbonate at High Pressure. *J. Chem. Eng. Data* **2002**, *47*, 282−285.

(5) Wagner, Z. Vapor-Liquid Equilibrium at High Pressure in the System Containing Carbon Dioxide and Propyl Acetate. *Fluid Phase Equilib.* **1995**, *110*, 175−182.

(6) Ismadji, S.; Bhatia, S. K. Solubility of Selected Esters in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **2003**, *27*, 1−11.

(7) Lentz, H.; Zeuner, V. Phase Diagrams of Molar Volume against Mole Fraction at Given Temperatures and Pressures for {x_A-Ar+x_BXe+(1-x_A-x_B)NH_3}. *J. Chem. Thermodyn.* **1995**, *27*, 997−1015.

(8) Peng, D. Y.; Robinson, D. B. A new Tow-constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(9) Soave, G. Improvement of the Van Der Waals Equation of State. *Chem. Eng. Sci.* **1984**, *39*, 357−361.

(10) Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: Singapore, 1986.

(11) Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(12) *IMSL, the IMSL Library*; IMSL Inc.: Houston, TX, 1979.

(13) Wagner, Z. Vapor-Liquid Equilibrium in the Carbon Dioxide-Ethyl Propanoete System at Pressures from 2 to 9 MPa and Temperatures from 303 to 323 K. *Fluid Phase Equilib.* **1995**, *112*, 125−129.

Received for review November 7, 2003. Accepted August 18, 2004.

JE034224J